# What is claimed is:

1. A formulation comprising at least one granulate containing

a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound, based on the total weight of the granulate,

b) from 10 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, based on the total weight of the granulate,

c) from 15 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof, based on the total weight of the granulate,

d) from 0 to 10 % by weight of at least one further additive, based on the total weight of the granulate, and

e) from 3 to 15 % by weight water, based on the total weight of the granulate.

- 2. A formulation according to claim 1, wherein the granulate comprises, as phthalocyanine compound, at least one water-soluble Zn(II), Fe(II), Ca(II), Mg(II), Na(I), K(I), AI, Si(IV), P(V), Ti(IV), Ge(IV), Cr(VI), Ga(III), Zr(IV), In(III), Sn(IV) or Hf(VI) phthalocyanine compound.
- 3. A formulation according to either claim 1 or claim 2, wherein the granulate comprises at least one phthalocyanine compound of formula

(1a) 
$$\left[Me\right]_{q}\left[PC\right]\left[Q_{1}\right]_{r}^{+}A_{s}^{-}$$
 or (1b)  $\left[Me\right]_{q}\left[PC\right]\left[Q_{2}\right]_{r}$ 

### wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z<sub>1</sub>; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

- Z<sub>1</sub> is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;
- q is 0, 1 or 2;
- r is from 1 to 4;
- Q<sub>1</sub> is a sulfo or carboxy group; or is a radical of formula  $-SO_2X_2-R_6-X_3^+$ ;  $-O-R_6-X_3^+$ ; or  $-(CH_2)_1-Y_1^+$ ;

### wherein

R<sub>6</sub> is branched or unbranched C<sub>1</sub>-C<sub>8</sub>alkylene; or 1,3- or 1,4-phenylene;

X<sub>2</sub> is -NH-; or -N-C<sub>1</sub>-C<sub>5</sub>alkyl-;

X<sub>3</sub><sup>+</sup> is a group of formula

$$\begin{array}{c} \stackrel{R_7}{\overset{}{\overset{}{\stackrel{}{\underset{}}{\stackrel{}}{\stackrel{}}}}} = \stackrel{R_{10}}{\overset{}{\overset{}{\stackrel{}}{\stackrel{}}}} = \stackrel{R_{10}}{\overset{}{\overset{}}{\stackrel{}}} = \stackrel{R_{10}}{\overset{}{\overset{}{\stackrel{}}{\stackrel{}}}} = \stackrel{R_{10}}{\overset{}{\overset{}}} = \stackrel{R_{10}}{\overset{}{\stackrel{}}} = \stackrel{R_{10}}{\overset{}{\stackrel{}}{\stackrel{}}} = \stackrel{R_{10}}{\overset{}} = \stackrel{$$

and, in the case where  $R_6 = C_1-C_8$ alkylene, may also be a group of formula

$$-N^{+} A_{1} ; -N^{+} B_{1} ; -N^{+} N ; -S^{+} = C N - R_{12}R_{13} ; or -S^{+}_{15};$$

$$R_{14}$$
  $N-R_{12}R_{13}$   
 $R_{15}$  is a group of formula  $R_{15}$   $R_{15}$   $R_{15}$   $R_{15}$   $R_{15}$   $R_{15}$ 

t is 0 or 1;

in which above formulae,

 $R_7$  and  $R_8$  are each independently of the other  $C_1\text{-}C_8\text{alkyl};$ 

R<sub>9</sub> is C<sub>1</sub>-C<sub>6</sub>alkyl; C<sub>5</sub>-C<sub>7</sub>cycloalkyl; or NR<sub>11</sub>R<sub>12</sub>;

 $R_{10}$  and  $R_{11}$  are each independently of the other  $C_1\text{-}C_5\text{alkyl};$ 

 $R_{12}$  and  $R_{13}$  are each independently of the other hydrogen or  $C_1\text{-}C_5$ alkyl;

 $R_{14}$  and  $R_{15}$  are each independently of the other unsubstituted or hydroxy-, cyano-, carboxy-,  $C_1$ - $C_6$ alkoxy-carbonyl-,  $C_1$ - $C_6$ alkoxy-, phenyl-, naphthyl- or pyridyl-substituted  $C_1$ - $C_6$ alkyl;

u is from 1 to 6;

contain one or two further nitrogen atoms as ring members, and

B<sub>1</sub> is the balance of a saturated 5- to 7-membered nitrogen heterocycle which may contain
 1 or 2 further nitrogen, oxygen and/or sulfur atoms as ring members;

Q<sub>2</sub> is hydroxy; C<sub>1</sub>-C<sub>22</sub>alkyl; branched C<sub>3</sub>-C<sub>22</sub>alkyl; C<sub>2</sub>-C<sub>22</sub>alkenyl; branched C<sub>4</sub>-C<sub>22</sub>alkenyl or a mixture thereof; C<sub>1</sub>-C<sub>22</sub>alkoxy; a sulfo or carboxy radical; a radical of formula

$$R_{16}$$
  $SO_2 X_4$   $R_{16}$   $SO_2 N_1$   $R_{18}$   $R_{19}$   $R_{19}$ 

$$-CH_2-Y_2$$
 ;  $-SO_2(CH_2)_v-OSO_3M$ ;  $-SO_2(CH_2)_v-SO_3M$ ;  $-SO_2(CH_2)_v-SO_3M$ ;

$$\begin{array}{c} R_{22} \\ -SO_2 - N - (CH_2)_v - OSO_3 M \end{array} \; ; \; -SO_2 - X_4 - (CH_2)_v - N \\ R_{19} \end{array} \; ; \label{eq:constraint}$$

$$-CH_{2}-Y_{2}-(CH_{2})_{v}-N \stackrel{R_{18}}{\underset{R_{19}}{\longleftarrow}}; \quad -(SO_{2}X_{1})_{w} \stackrel{Q}{\longleftarrow} \stackrel{N}{\underset{R_{19}}{\longleftarrow}} \stackrel{R_{18}}{\underset{R_{19}}{\longleftarrow}}; \quad -CH_{2}Y_{2} \stackrel{Q}{\longleftarrow} \stackrel{N}{\underset{R_{19}}{\longleftarrow}} \stackrel{R_{18}}{\underset{R_{19}}{\longleftarrow}};$$

a branched alkoxy radical of formula 
$$CH_2 - (O)_a (CH_2)_b - (OCH_2 CH_2)_c - B_2$$

$$CH_2 - (O)_a (CH_2)_b - (OCH_2 CH_2)_c - B_2$$

$$CH_2 - (O)_a (CH_2)_b - (OCH_2 CH_2)_c - B_2$$

- $(T_1)_d$ - $(CH_2)_b(OCH_2CH_2)_a$ - $B_3$  or an ester of formula COOR<sub>23</sub>,

wherein

B<sub>2</sub> is hydrogen; hydroxy;  $C_1$ - $C_{30}$ alkyl;  $C_1$ - $C_{30}$ alkoxy; - $CO_2$ H; - $CH_2$ COOH;  $SO_3$ - $M_1$ ; - $OSO_3$ - $M_1$ ; - $OPO_3$ - $M_1$ ; - $OPO_3$ - $M_1$ ; or a mixture thereof;

B<sub>3</sub> is hydrogen; hydroxy; -COOH; -SO<sub>3</sub>·M<sub>1</sub>; -OSO<sub>3</sub>·M<sub>1</sub>; or C<sub>1</sub>-C<sub>6</sub>alkoxy;

M<sub>1</sub> is a water-soluble cation;

 $T_1$  is -O-; or -NH-;

 $X_1$  and  $X_4$  are each independently of the other -O-; -NH-; or -N-C<sub>1</sub>-C<sub>5</sub>alkyl;

- R<sub>16</sub> and R<sub>17</sub> are each independently of the other hydrogen; a sulfo group or a salt thereof; a carboxy group or a salt thereof, or a hydroxy group, at least one of the radicals R<sub>16</sub> and R<sub>17</sub> being a sulfo or carboxy group or a salt thereof,
- Ŷ₂ is -O-; -S-; -NH- or -N-C<sub>1</sub>-C₅alkyl;
- R<sub>18</sub> and R<sub>19</sub> are each independently of the other hydrogen; C<sub>1</sub>-C<sub>6</sub>alkyl; hydroxy-C<sub>1</sub>-C<sub>6</sub>alkyl; cyano-C<sub>1</sub>-C<sub>6</sub>alkyl; sulfo-C<sub>1</sub>-C<sub>6</sub>alkyl; carboxy- or halo-C<sub>1</sub>-C<sub>6</sub>alkyl; unsubstituted or halo-, C<sub>1</sub>-C<sub>4</sub>alkyl-, C<sub>1</sub>-C<sub>4</sub>alkoxy-, sulfo- or carboxy-substituted phenyl; or R<sub>18</sub> and R<sub>19</sub>, together with the nitrogen atom to which they are bonded, are a saturated 5- or 6-membered heterocyclic ring which may additionally contain a further nitrogen or oxygen atom as ring member;

R<sub>20</sub> and R<sub>21</sub> are each independently of the other a C<sub>1</sub>-C<sub>6</sub>alkyl or aryl-C<sub>1</sub>-C<sub>6</sub>alkyl radical;

- R<sub>22</sub> is hydrogen; or unsubstituted or halo-, hydroxy-, cyano-, phenyl-, carboxy-, C<sub>1</sub>-C<sub>6</sub>- alkoxy-carbonyl- or C<sub>1</sub>-C<sub>6</sub>alkoxy-substituted C<sub>1</sub>-C<sub>6</sub>alkyl;
- R<sub>23</sub> is C<sub>1</sub>-C<sub>22</sub>alkyl; branched C<sub>4</sub>-C<sub>22</sub>alkyl; C<sub>1</sub>-C<sub>22</sub>alkenyl or branched C<sub>4</sub>-C<sub>22</sub>alkenyl; C<sub>3</sub>-C<sub>22</sub>-glycol; C<sub>1</sub>-C<sub>22</sub>alkoxy; branched C<sub>4</sub>-C<sub>22</sub>alkoxy; or a mixture thereof;
- M is hydrogen; or an alkali metal ion or ammonium ion,
- Z<sub>2</sub> is a chlorine ion, bromine ion, alkylsulfate ion or aralkylsulfate ion;
- a is 0 or 1;
- b is from 0 to 6;
- c is from 0 to 100;
- d is 0 or 1;
- e is from 0 to 22;
- v is an integer from 2 to 12;
- w is 0 or 1; and
- A is an organic or inorganic anion,

and

in the case of monovalent anions A is equal to r and in the case of polyvalent anions is  $\leq r$ , it being necessary for A<sub>s</sub> to balance the positive charge; and when  $r \neq 1$ , the radicals Q<sub>1</sub> may be identical or different,

and wherein the phthalocyanine ring system may also contain further solubility-imparting groups.

4. A formulation according to claim 3, wherein the granulate comprises at least one

phthalocyanine compound of formula (2a) [Me] 
$$q^{PC} \sim (SO_3M)_{r_i} (SO_2X_2-R_6-X_3^+)_{r_2} A_s$$
,

wherein

Me, q, PC, X2, X3 and R6 are as defined for formula (1a),

M is hydrogen; or an alkali metal ion, ammonium ion or amine salt ion;

and the sum of the numbers r<sub>1</sub> and r<sub>2</sub> is from 1 to 4, and

As exactly balances the positive charge of the remainder of the molecule, or of formula

(3) [Me] 
$$q$$
 [PC]  $SO_2NHR_6'-X_3'^+$  A'],

wherein

Me, q and PC are as defined for formula (1a),

R<sub>6</sub>' is C<sub>2</sub>-C<sub>6</sub>alkylene;

r is a number from 1 to 4;

$$X_3$$
' is a group of formula  $N_1 = N_1 = N_2 = N_3$ ;  $N_2 = N_3 = N_3$ 

or 
$$-N^{+}$$
  $N$ 

wherein

R<sub>7</sub> and R<sub>8</sub> are each independently of the other unsubstituted or hydroxy-, cyano-, halo- or phenyl-substituted C<sub>1</sub>-C<sub>4</sub>alkyl;

R<sub>9</sub> is R<sub>7</sub>; cyclohexyl or amino;

R<sub>11</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl;

R<sub>21</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl; C<sub>1</sub>-C<sub>4</sub>alkoxy; halogen; carboxy; C<sub>1</sub>-C<sub>4</sub>alkoxy-carbonyl or hydroxy; and

A' is a halide ion, alkylsulfate ion or arylsulfate ion;

it being possible for the radicals -SO₂NHR'<sub>s</sub>-X₃'<sup>+</sup>A to be identical or different.

5. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula

(4) 
$$\left[Me\right]_{q}\left[PC\right]\left[SO_{3}-Y_{3}\right]_{r}$$

### wherein

PC is the phthalocyanine ring system;

Me is Zn; Fe(II); Ca; Mg; Na; K; Al-Z<sub>1</sub>; Si(IV); P(V); Ti(IV); Ge(IV); Cr(VI); Ga(III); Zr(IV); In(III); Sn(IV) or Hf(VI);

- Z<sub>1</sub> is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion;
- q is 0; 1; or 2;
- Y<sub>3</sub>' is hydrogen; or an alkali metal ion or ammonium ion; and
- r is any number from 1 to 4.
- 6. A formulation according to claim 5, wherein the granulate comprises at least one phthalocyanine compound of formula (4) wherein

Me is Zn or Al-Z<sub>1</sub>; and

- Z<sub>1</sub> is a halide ion, sulfate ion, nitrate ion, acetate ion or hydroxy ion.
- 7. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula

(5) 
$$[Me]_q[PC]$$
  $SO_2$ -NH- $[CH_2]_q$ -N $[R_{18}]$ 

## wherein

PC, Me and q are as defined for formula (4);

- R<sub>17</sub>' and R<sub>18</sub>' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C<sub>1</sub>-C<sub>6</sub>alkyl; hydroxy-C<sub>1</sub>-C<sub>6</sub>alkyl; cyano-C<sub>1</sub>-C<sub>6</sub>alkyl; sulfo-C<sub>1</sub>-C<sub>6</sub>alkyl; carboxy-C<sub>1</sub>-C<sub>6</sub>alkyl or halo-C<sub>1</sub>-C<sub>6</sub>alkyl or, together with the nitrogen atom, form a morpholine ring;
- q' is an integer from 2 to 6; and
- r is a number from 1 to 4;
- it being possible, when r > 1, for the radicals  $-SO_2$ -NH- $(CH_2)_{q'}$  N present in the  $R_{1n}$

molecule to be identical or different.

8. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula

(6) 
$$\begin{bmatrix} SO_3 - Y_3 \end{bmatrix}_{r}$$

$$SO_2 \begin{bmatrix} NH - (CH_2)q \end{bmatrix}_{m'} R_{17},$$

wherein

PO; Me and q are as defined for formula (4);

Y'<sub>3</sub> is hydrogen; or an alkali metal ion or ammonium ion,

q' is an integer from 2 to 6;

R<sub>17</sub>' and R<sub>18</sub>' are each independently of the other hydrogen; phenyl; sulfophenyl; carboxyphenyl; C<sub>1</sub>-C<sub>6</sub>alkyl; hydroxy-C<sub>1</sub>-C<sub>6</sub>alkyl; cyano-C<sub>1</sub>-C<sub>6</sub>alkyl; sulfo-C<sub>1</sub>-C<sub>6</sub>alkyl; carboxy-C<sub>1</sub>-C<sub>6</sub>alkyl or halo-C<sub>1</sub>-C<sub>6</sub>alkyl or, together with the nitrogen atom, form a morpholine ring,

m' is 0 or 1; and

r and  $r_1$  are each independently of the other any number from 0.5 to 3.5, the sum  $r + r_1$  being a minimum of 1 and a maximum of 4.

9. A formulation according to claim 3, wherein the granulate comprises at least one phthalocyanine compound of formula

wherein

R<sub>24</sub> is hydroxy; C<sub>1</sub>-C<sub>22</sub>alkyl; branched C<sub>4</sub>-C<sub>22</sub>alkyl; C<sub>1</sub>-C<sub>22</sub>alkenyl; branched C<sub>4</sub>-C<sub>22</sub>alkenyl or a mixture thereof; C<sub>1</sub>-C<sub>22</sub>alkoxy; a sulfo or carboxy radical; a radical of formula

$$-SO_{2} \cdot X_{4} - X_{16} + X$$

-(T<sub>1</sub>)<sub>d</sub>-(CH<sub>2</sub>)<sub>b</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>a</sub>-B<sub>3</sub> or an ester of formula COOR<sub>23</sub>; and

U is  $[Q_1]_r^+A_s^-$ ; or  $Q_2$ ;

 $R_{16}$ ,  $R_{17}$ ,  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$ ,  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{23}$ ,  $R_{24}$ ,  $R_{25}$ ,  $R_{2$ 

**10.** A formulation according to any one of claims 1 to 9, wherein the granulate contains from 4 to 30 % by weight of at least one phthalocyanine compound.

- 11. A formulation according to any one of claims 1 to 9, wherein the granulate contains from 5 to 20 % by weight of at least one phthalocyanine compound.
- 12. A formulation according to any one of claims 1 to 11, wherein the granulate contains from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer.
- 13. A formulation according to any one of claims 1 to 11, wherein the granulate contains from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer.
- 14. A formulation according to any one of claims 1 to 13, wherein the granulate comprises, as anionic dispersing agent, one or more condensation products from the following group: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated biphenyls or biphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylnaphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalenemethanesulfonates, ligno- or oxyligno-sulfonates and heterocyclic polysulfonic acids.
- 15. A formulation according to any one of claims 1 to 13, wherein the granulate comprises, as anionic dispersing agent, a condensation product from the following group: condensation products of naphthalenesulfonic acids with formaldehyde, sodium salts of polymerised organic sulfonic acids, (mono-/di-)alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerised alkylbenzenesulfonic acid, lignosulfonates, oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl.
- **16.** A formulation according to any one of claims 1 to 15, wherein the granulate comprises, as water-soluble (but not necessarily film-forming) polymer, one or more compounds from the following group:

BANGAR BURNARA MARANGANAN

gelatins, polyacrylates, polymethacrylates, copolymers of ethyl acrylate, methyl methacrylate and methacrylic acid (ammonium salt), polyvinylpyrrolidones, vinylpyrrolidones, vinyl with long-chain olefins. poly(vinylvinylpyrrolidone acetates, copolymers of pyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methterpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyltrimethylammonium chloride, terpolymers of caprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethyl cellulose, hydroxymethyl cellulose, polyvinyl alcohols, hydrolysed and non-hydrolysed polyvinyl acetate, copolymers of maleic acid with unsaturated hydrocarbons and also mixed polymerisation products of the mentioned polymers, polyethylene glycol (MW = 4000 -20 000), copolymers of ethylene oxide with propylene oxide (MW > 3500), condensation products (block polymerisation products) of alkylene oxide, especially propylene oxide, copolymers of vinylpyrrolidone with vinyl acetate, ethylene oxide-propylene oxide addition products with diamines, especially ethylenediamine, polystyrenesulfonic acid, polyethylenesulfonic acid, copolymers of acrylic acid with sulfonated styrenes, gum arabic, hydroxypropyl methylcellulose, sodium carboxymethyl cellulose, hydroxypropyl methylcellulose phthalate, maltodextrin, starch, sucrose, lactose, enzymatically modified and subsequently hydrated sugars, as are obtainable under the name "Isomalt", cane sugar, polyaspartic acid and tragacanth.

- 17. A formulation according to any one of claims 1 to 15, wherein the granulate comprises, as water-soluble polymer, a compound from the following group: carboxymethyl cellulose, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatins, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, maltodextrins, polyaspartic acid and also polyacrylates and polymethacrylates.
- **18.** A formulation according to any one of claims 1 to 17, wherein the granulate contains from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid and/or a salt thereof.

- 19. A formulation according to any one of claims 1 to 17, wherein the granulate contains from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-molecular-weight organic acid and/or a salt thereof.
- 20. A formulation according to claim 19, wherein the granulate comprises, as inorganic salt and/or low-molecular-weight organic acid and/or a salt thereof, at least one compound from the group consisting of carbonate; hydrogen carbonate; phosphate; polyphosphate; sulfate; silicate; sulfite; borate; halide; pyrophosphate; aliphatic carboxylic acid having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylate; phytate; phosphonate; aminopolyphosphonate; aminopolycarboxylate; phytate; phosphonate; polycarboxylate; water-soluble polysiloxane; and a water-soluble salt used in washing agent and/or washing agent additive formulations.

BETARENDE LINE VIE HOVERED

- 21. A formulation according to claim 20, wherein the granulate comprises, as low-molecular-weight organic acid, an aliphatic  $C_2$ - $C_{12}$ polycarboxylic acid or a salt thereof.
- 22. A formulation according to claim 21, wherein the granulate comprises, as low-molecular-weight organic acid, oxalic acid, tartaric acid, acetic acid, propionic acid, succinic acid, maleic acid, citric acid, formic acid, gluconic acid, p-toluenesulfonic acid, terephthalic acid, benzoic acid, phthalic acid, acrylic acid and/or polyacrylic acid and/or a salt thereof.
- 23. A formulation according to any one of claims 1 to 22, wherein the granulate contains from 0 to 5 % by weight of at least one further additive.
- 24. A formulation according to claim 23, wherein the granulate comprises a wetting agent, a disintegrant, a filler, a water-insoluble or water-soluble dye or pigment, and/or a dissolution accelerator, an optical brightener, a zeolite, talc, powdered cellulose, fibrous cellulose, microcrystalline cellulose, kaolin, TiO<sub>2</sub>, SiO<sub>2</sub> and/or magnesium trisilicate.
- 25. A formulation according to any one of claims 1 to 24, wherein the granulate consists of a) from 4 to 30 % by weight of at least one water-soluble phthalocyanine compound as defined in any one of claims 2 to 9,

WO 2004/022693 опредержания предутивания на настра объектический принастический принастический на настранествення в настранест

> b) from 12 to 60 % by weight of at least one anionic dispersing agent and/or at least one water-soluble organic polymer, as defined in either claim 14 or

> > claim 15,

c) from 20 to 75 % by weight of at least one inorganic salt and/or at least one low-

molecular-weight organic acid or a salt thereof, as defined in

any one of claims 20 to 22,

d) from 0 to 5 % by weight at least one further additive as defined in claim 24, and

water, based on the total weight of the granulate. e) from 3 to 15 % by weight

26. A formulation according to any one of claims 1 to 24, wherein the granulate consists of

of at least one water-soluble phthalocyanine compound as a) from 5 to 20 % by weight

one continue of claims 2 to 9; in the continue of claims 2 to 9; in the continue of claims 2 to 9;

b) from 12 to 55 % by weight of at least one anionic dispersing agent and/or at least one

water-soluble organic polymer, as defined in either claim 14 or

claim 15,

c) from 25 to 70 % by weight of at least one inorganic salt and/or at least one low-

molecular-weight organic acid or a salt thereof, as defined in

any one of claims 20 to 22,

d) from 0 to 5 % by weight at least one further additive as defined in claim 24, and

e) from 3 to 15 % by weight water, based on the total weight of the granulate.

27. A formulation according to any one of claims 1 to 24, wherein the granulate consists of

a) from 2 to 50 % by weight

of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above,

b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalenesulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkylnaphthalenesulfonates; polyalkylated polynuclear arylsulfonates; sodium salts of polymerised alkylbenzenesulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl;

and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of vinylpyrrolidone and vinyl acetate; maltodextrins; polyaspartic acid; polyacrylates and polymethacrylates, and

c) from 15 to 75 % by weight

of at least one inorganic salt and/or at least one low-molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites; borates; halides; pyrophosphates; aliphatic carboxylic acids having a total number of from 1 to 12 carbon atoms, which are unsubstituted or substituted by hydroxy and/or by amino; aminopolycarboxylates; phytates; phosphonates; aminopolyphosphonates; aminoalkylenepoly-(alkylenephosphonates); polyphosphonates; polycarboxylates; water-soluble polysiloxanes; and water-soluble salts used in washing agent and/or washing agent additive formulations, and

d) from 0 to 10 % by weight

of at least one further additive from the group consisting of wetting agents; disintegrants; fillers; water-insoluble or water-soluble dyes or pigments; dissolution accelerators; optical brighteners; aluminium silicates; talc; kaolin; TiO<sub>2</sub>, SiO<sub>2</sub>; and magnesium trisilicate, and

e) from 3 to 15 % by weight

water, based on the total weight of the granulate.

- 28. A formulation according to any one of claims 1 to 27, wherein the granulate has an average particle size of < 500 μm.
- 29. A formulation according to any one of claims 1 to 27, wherein the granulate has an average particle size of from 40 to 400  $\mu m$ .
- **30.** Use of a formulation according to any one of claims 1 to 29 as a washing agent composition, washing agent additive or additive concentrate.

31. Use of a formulation, according to claim 30, as or in a pre- and/or after-treatment agent, stain-removing salt, washing-power enhancer, fabric conditioner, bleaching agent and/or UV-protection enhancer.

32. Use of a formulation, according to claim 30, in the form of a powder, (super-)compact powder, single- or multi-layer tablet (tab), bar, block, sheet, paste, washing agent gel, or in the form of a powder, paste, gel or liquid packed in capsules or in pouches (sachets).

33. A washing agent formulation according to any one of claims 1 to 29 consisting of

I) from 5 to 70 % A)

of at least one anionic surfactant and/or B) at least one non-ionic surfactant, based on the total weight of the washing agent formulation,

II) from 5 to 60 % C)

of at least one builder substance, based on the total

weight of the washing agent formulation,

III) from 0 to 30 % D)

of at least one peroxide and, optionally, at least one activator, based on the total weight of the washing agent

formulation, and

IV) from 0.001 to 1 % E)

of at least one granulate as defined in any one of claims 1 to 29,

and

V) from 0 to 60 % F)

of at least one further additive, and

VI) from 0 to 5 % G)

water.

34. A washing agent formulation according to claim 33, consisting of

I) from 5 to 70 % A)

of at least one anionic surfactant from the group consisting of alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical; alkylnaphthalenesulfonates having from 6 to 16 carbon atoms in the alkyl radical; and alkali metal sarcosinates of the formula R-CO-N(R<sub>1</sub>)-CH<sub>2</sub>COOM<sub>1</sub>,

wherein R is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical,

R<sub>1</sub> is C<sub>1</sub>-C<sub>4</sub>alkyl and

M<sub>1</sub> is an alkali metal and/or

B) at least one non-ionic surfactant from the group consisting of condensation products of from 3 to 8 mols

of ethylene oxide with 1 mol of primary alcohol containing from 9 to 15 carbon atoms,

II) from 5 to 60 % C)

of a builder substance from the group consisting of alkali metal phosphates; carbonates; hydrogen carbonates; silicates; aluminium silicates; polycarboxylates; polycarboxylic acids; organic phosphonates and aminoalkylenepoly(alkylenephosphonates), and

III) from 0 to 30 % D)

of a peroxide from the group consisting of organic mono- or poly-peroxides; organic peracids and salts thereof; persulfates; perborates; percarbonates and persilicates,

IV) from 0.001 to 1 % E) of a granulate which contains

a) from 2 to 50 % by weight of at least one water-soluble phthalocyanine compound of formula (2a), (3), (4), (5), (6) and/or (7) defined above, and

b) from 10 to 60 % by weight of at least one anionic dispersing agent from the group consisting of condensation products of naphthalenesulfonic acid with formaldehyde; sodium salts of polymerised organic sulfonic acids; (mono-/di-)alkylnaphthalenesulfonates; polyalkylated polynuclear arylsulfonates; sodium salts of polymerised alkylbenzenesulfonic acids; lignosulfonates; oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethylbiphenyl;

and/or at least one water-soluble organic polymer from the group consisting of carboxymethyl cellulose; polyacrylamides; polyvinyl alcohols; polyvinylpyrrolidones; gelatins; hydrolysed polyvinyl acetates; copolymers of maltodextrins; acetate; vinylpyrrolidone and vinyl polyaspartic acid; polyacrylates and polymethacrylates, and

s response to the second of th molecular-weight organic acid or a salt thereof from the group consisting of carbonates; hydrogen carbonates; phosphates; polyphosphates; sulfates; silicates; sulfites;

- 37. A process according to claim 35, wherein the removal of water is performed by spraydrying with direct return of the fines of the solid material to the spray zone.
- **38.** A process according to claim 35, wherein the removal of water is performed in a fluidised spray-dryer.
- 39. A process according to claim 35, wherein the removal of water is performed in a fluidised bed granulator.
- **40.** A process according to any one of claims 35 to 39, wherein a phthalocyanine solution purified of organic by-products by a membrane separation procedure is used.
- **41.** A granulate as defined in any one of claims 1 to 29 with the proviso that it does not contain ethoxylated stearyldiphenyloxyethyldiethyltriamine.
- **42.** A granulate as defined in claim 41 with the proviso that it is not encapsulated and it has a substantially homogeneous distribution of ingredients.
- 43. Treatment of textiles using a formulation according to any one of claims 1 to 34.